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A High Potential of Biomass Leaves Waste for Porous Activated Carbon Nanofiber/Nanosheet as Electrode Material of Supercapacitor

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Abstract. Since porous carbon materials derived from biomass, with low cost, abundant and sustainable, relatively easy fabrication, high electrical conductivity, large specific surface area (SSA), surface morphology with nanomaterial structures, and superior electrochemical stability have attracted attention which are strong and highly trusted to be a candidate for the electrode material of supercapacitor energy storage. This study highlighted recent laboratory-scale methods for preparing activated carbon nanostructures from leaves biomass wastes. Four types of focused leaves waste including acacia leaves, pineapple leaves, and *Terminalia catappa* leaves (TCL), and *Pandanus tectorius* leaves (PTL). Leave wastes were converted into activated carbon by KOH activation and one-stage integrated pyrolysis both of carbonization and physical activation. Symmetric supercapacitor electrode were performed with sandwich-type in monolith form without adhesive materials. Among the raw materials found in this study, nanofiber structures dominated the surface morphology of carbon monolith, especially in acacia leaves, pineapple leaves, and TCL. Interestingly, the same basic material of TCL could perform two different nanostructures including nanofiber and nanosheet. In addition, the percentages of carbon and oxygen contents in the sample were also provided. Furthermore, supercapacitor cells exhibited the highest specific capacitance are activated carbon derived from pineapple leaves as high as 150 F g^{-1} in $1 \text{ M H}_2\text{SO}_4$ aqueous electrolyte at a low scanning rate of 1 mV s^{-1} . Finally, these results confirmed that leaves biomass wastes have high potential as a raw material of activated carbon nanofiber/nanosheet structure to be applied in supercapacitor electrodes.

1. Introduction

The activated carbon nanostructures with various morphologies have attracted attention due to their superior physical and chemical properties for applications such as supercapacitors [1], batteries, catalysis, and sensors. The main reasons for using activated carbon in various fields are its relatively greater abundance, easier fabrication, lower costs, and negligible health and environmental hazards [2,3]. The biggest source of activated carbon material is biomass due to high lignocellulose compound which including hemicellulose, cellulose, and lignin [4]. The basic components of plant biomass including cellulose, hemicellulose, lignin, plant protein, plant lipids offer a basic skeleton structure and abundant functional groups for the carbons.

Biomass is converted to activated carbon through several steps such as carbonization, chemical activation, and physical activation, or a combination of all three [5,6]. These steps could decompose cellulose, hemicellulose, and lignin and evaporate volatile compounds to produce fixed carbon.



Hemicellulose and cellulose are less stable in thermal decomposition compared to lignin and contribute to low carbon yields [7]. However, the components of hemicellulose, lignin, and cellulose contribute to fixed carbon porosity [4]. Interestingly these three components contribute to producing nanostructures on activated carbon. Through thermal treatment, cellulose contributes to the structure of nano/hollow fiber and nanotubes while hemicellulose and lignin exhibit nanosheet and nanosphere structures [8–10]. These nanostructures play a role in providing micro, meso, and macropore interconnections to increase the energy density of supercapacitors.

Till now, many research articles have reported the potential of biomass to obtain nanostructures in biochar. Cai et al. reported nanosheet structure of activated carbon from the biomass material *Moringa oleifera* stem waste. It exhibits a high surface area of $2250 \text{ m}^2 \text{ g}^{-1}$ with hierarchically porous nanosheets and exceptional specific capacitance of 283 F g^{-1} [11]. A similar structure was also reported by several researchers from different biomass wastes such as *Helianthus annuus* seed [12], soybean milk [13], and corn cob ash [14]. They stated that the nanosheet contributes to providing micro and mesopores interconnection and that it increases the performance of electrode material for supercapacitors. Meanwhile, various biomass wastes demonstrate the existence of nanofiber structures with extraordinary physical properties to support the performance of supercapacitor electrodes. The structure of nano/hollow fiber is performed on activated carbon *Hexagonia apiaria* with a specific surface area of $1280 \text{ m}^2 \text{ g}^{-1}$. This structure can increase specific capacitance from 171 to 324 F g^{-1} [15]. A similar structure is also found in wheat-straw biomass [16] and banana stem [17]. Other nanostructures such as nanotubes and nanosphere have also been reported from biomass origin materials of Areca nut seeds [18] and *Areca catechu* husk [19]. However, all of these nanostructures are obtained by complex methods, multi-step processes, and the addition of synthetic materials, composites, metal frameworks, and templates. In addition, not all biomass displays nanostructure in activated carbon material. Therefore, it is necessary to know the biomass criteria that allows producing nanostructures with a simple method and does not require the addition of other synthetic materials.

In this study, we review the potential of biomass leaves wastes as nanostructured activated carbon as electrode material for supercapacitors. Different leaf wastes have been selected such as acacia leaves, *Pandanus tectorius* leaves, *Terminalia cattapa* leaves, and pineapple leaves. Preparation of activated carbon is carried out as simple as possible and does not use composite materials, polymers, metal frameworks or templates. Pure leaf waste is pyrolysis and chemically activated. One-stage integrated pyrolysis was chosen for the carbonization and physical activation. In addition, activated carbon is tested in the form of monoliths/pellets without the addition of adhesives such as PTFE or pVdF. The results of this review indicate the high potential of leaf waste to produce nanostructured activated carbon with a more efficient and effective method for supercapacitor electrode material.

2. Materials and Methods

The preparation of activated carbon nanostructures made from leaves waste is focused on four different types such as acacia leaves, *Pandanus tectorius* leaves (PTL), *Terminalia cattapa* leaves (TCL), and pineapple leaves. All leaves wastes were collected from the Pekanbaru area. The conversion process consists of three main steps, including (i) initial treatment, (ii) chemical activation, and (iii) one-stage integrated pyrolysis both carbonization and physical activation. (i) Initial treatment began with the collection, cleaning, and drying of the raw material. Subsequently, the sample was pre-carbonized in a vacuum oven for 2.5 hours at a temperature of 250°C . The pre-carbonized sample was converted in powder through a grinding process. The sample powder was sieved to obtain a uniform particle size <53 microns. (ii) Chemical activation is focused on the KOH activator agent with relatively varying concentrations, as previously reported [20–23]. KOH activated sample powder was converted in the form of a monolith/pellet using a hydraulic press without the addition of an adhesive material. (iii) One-stage integrated pyrolysis was chosen as a pyrolysis process that could combine carbonization and physical activation processes. This method is considered more effective and efficient in producing fixed carbon through carbonization and activation. A total of 20 carbon monoliths are inserted into the furnace tube. Furthermore, carbonization is initiated at room temperature until it reaches a maximum temperature of 600°C in an N_2 gas environment then followed by physical activation to a high temperature in a CO_2 gas atmosphere for 2.5 hours. Finally,

carbon monoliths are neutralized using distilled water. In detail, the scheme for preparation of activated carbon monoliths is shown in Figure 1.

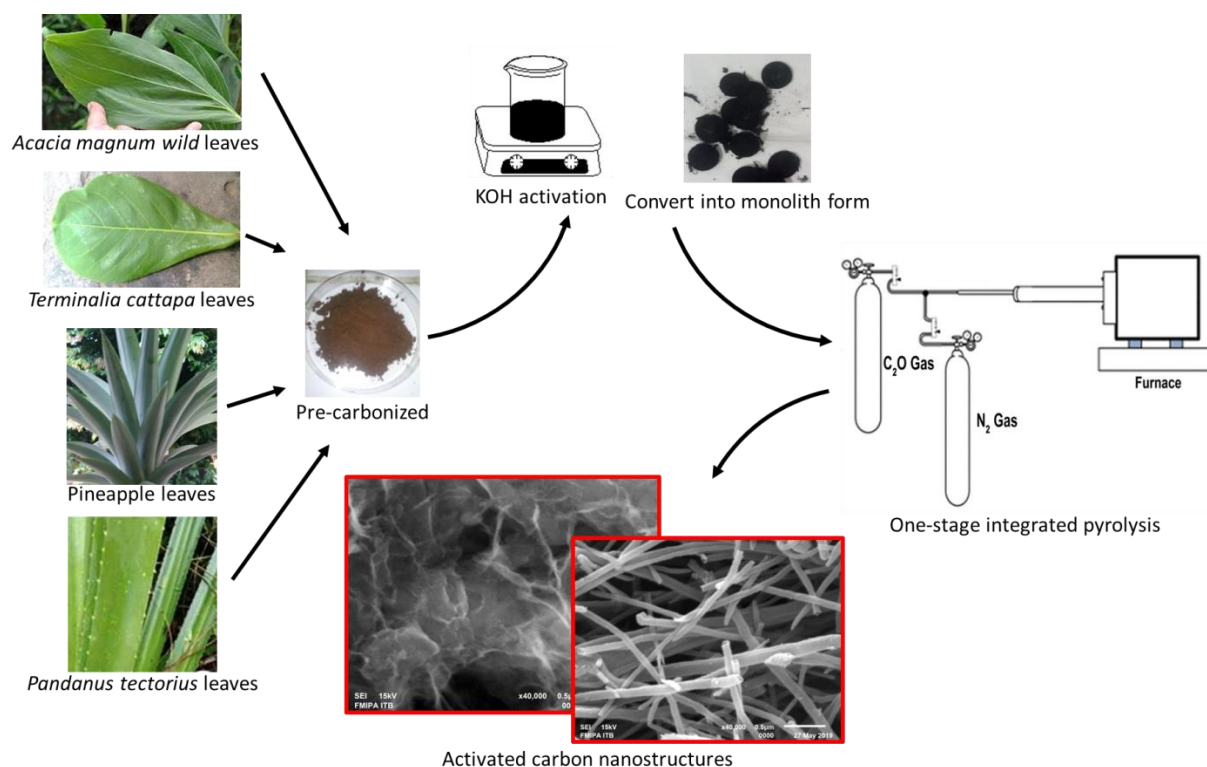


Figure 1. Schematic preparation of activated carbon nanostructures

The electrochemical behavior of activated carbon monoliths were evaluated using the cyclic voltammetry method. Supercapacitors are assembled in the sandwich form consisting of carbon nanostructured electrodes, separators, and electrolytes. The two-electrode system was selected to test the specific capacitance due closer to the real value than the three-electrode system. The electrolyte used is 1 M H_2SO_4 aqueous electrolyte with a duck eggshell membrane as a separator. Specific capacitance, energy density, and power density are evaluated based on standard equations.

3. Results and Discussion

Surface morphology is the main review for evaluating nanostructures on activated carbon monoliths for supercapacitor electrodes. The various nanostructures display different electrochemical activity and surface area for supercapacitor electrodes, including EDLC and pseudocapacitors. The variations in the nanostructure of activated carbon derived from biomass materials are influenced by raw materials, activating agents, and pyrolysis treatment to convert them to carbon fixed [7]. In general, biomass materials contain cellulose, hemicellulose, and lignin [4], which have the potential to develop into nanomaterial structures, including carbon nanosheets, nanofibers, nanotubes, and nanosphere. These structures provide natural heteroatom pores which benefit pseudocapacitive behaviour. The KOH activator is impregnated into the raw material to make porous carbon. The KOH activation process is carried out in one-stage integrated pyrolysis both carbonization and physical activation. During carbonization, low volatile molecular weights such as oxygen, nitrogen, and hydrogen are transformed into tar in the gas phase, which leads to the rearrangement of carbon atoms. Furthermore, physical activation in high temperatures facilitates the development of pores through the gasification reaction between char and CO_2 . Moreover, carbonization and physical activation in high temperatures facilitate the etched of lignocellulose compounds including hemicellulose, cellulose, and lignin. These three compounds contribute to providing nanostructures on activated carbon.

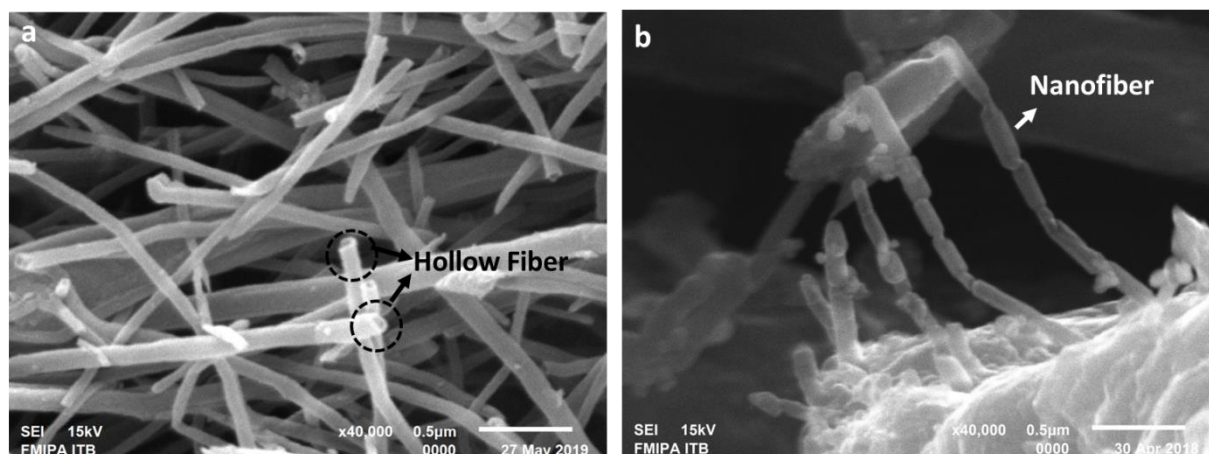


Figure 2. (a) SEM micrograph of acacia leaves, and (b) SEM micrograph of pineapple leaves

Acacia leaves show a surface morphology that is rich in nanofiber. Different physical activation temperatures indicate varying fiber densities. Acacia leaves were activated at a temperature of 850 °C showing high nanofiber density with a diameter around of 62-124 nm, see Figure 2(a). Furthermore, hollow fiber is also found in the morphology structure. The combination of nanofiber and hollow fiber makes it possible to provide numerous active pores for the diffusion of electrolyte ions on the electrode surface [24,25]. A similar morphology is also demonstrated by activated carbon monoliths derived from pineapple leaves that are physically activated at the same temperature of 850 °C which shown in Figure 2(b). The nanofiber diameter is relatively smaller around of 56-103 nm than acacia leaves. This is indicated that the physical activation at high temperatures, especially 850 °C, could decompose lignin and hemicellulose in cellulose in leaves biomass which contributes to producing activated carbon with nanofiber structures. In another study, the activated carbon of pineapple leaves performed nanosheet structures with open channel pores, as reported by Sodtipinta et al. [26,27].

Unlike *Terminalia cattapa* leaves (TCL) in Figure 3(a) and 3(b), activated carbon made from *Terminalia cattapa* leaves showed an interesting combination of nanostructures. At a carbonization temperature of 500 °C, TCL activated carbon features a nanofiber structure with a larger diameter around of 35-230 nm. However, at a higher carbonization temperature of 700 °C, nanosheets appear on the surface morphology of the activated carbon, see Figure 3b. It is possible that the carbonization temperature affects the decomposition of lignocellulose complex compounds and decomposes the cellulose and lignin, and evaporates hemicellulose. Cellulose is eroded at 500 °C giving rise to nanofiber structures. The application of higher carbonization temperatures around 700 °C could decomposes nanofibers and it's followed by erosion of lignin. This erosion of lignin is continued in the physical activation in high-temperature of 850 °C which allows the formation of nanosheets in activated carbon monoliths. The same analysis was also conveyed by several previous studies [11,28]. However, Monolithic activated carbon from *Pandanus tectorius* leaves does not show nanostructures on surface morphology. Although *Pandanus tectorius* leaves biomass is imregnated with KOH and carbonization and physical activation at the same temperature, as shown in Figure 3(c).

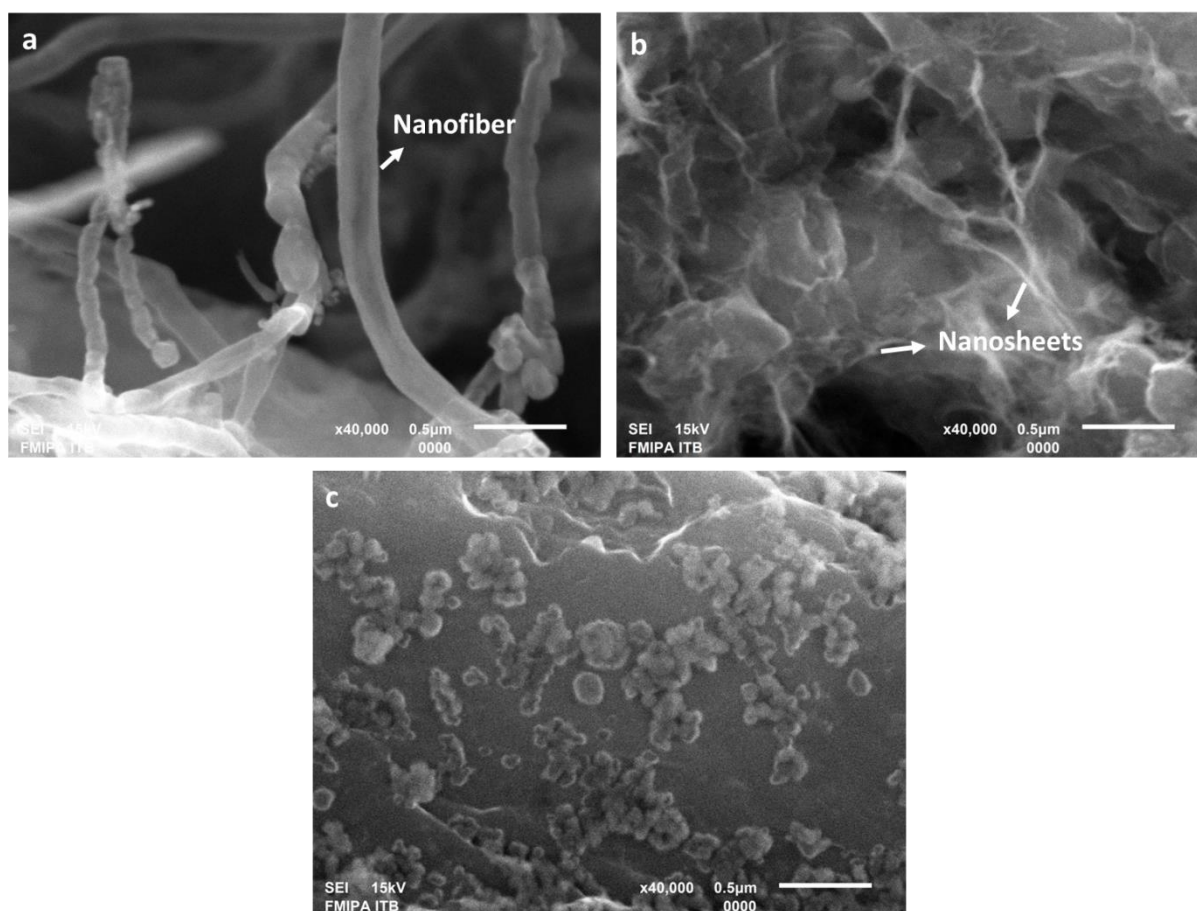


Figure 3. (a) SEM micrograph of TCL in carbonization temperature of 500 °C, (b) SEM micrograph of TCL in carbonization temperature of 700 °C, and (b) SEM micrograph of PTL

Moreover, Leaves wastes were prepared by the one-stage integrated pyrolysis and KOH activation has succeeded in obtaining relatively high carbon monoliths, as shown in table 1. In general carbon content is greater than 90% except TCL. These results confirmed that the one-stage integrated pyrolysis method is very effective to be used to convert leaves waste into carbon monoliths for electrodes supercapacitor. Furthermore, the samples also showed oxygen at low concentrations in the range of 3.50-13.49%. As well known, leaves biomass wastes, especially acacia leaves, pineapple leaves, PTL, and TCL are known to contain functional groups with a combination of carbon and oxygen, including phenol (C-OH), Quinone (C=O) or ether (COC), and carboxylic groups (COOH). In the pyrolysis process, oxygen is released due to low molecular weight and poor thermal stability [29]. However, higher oxygen content could be to increase the wettability and diffusion of electrolyte ions into the electrode pores [30].

Table 1. The percentages of carbon content and oxygen content for different leaves biomass waste

Raw material	Carbonization (°C)	Chemical activation	Physical activation (°C)	C (%)	O (%)	Refs
Acacia leaves	600	0.5 M KOH	850	92.62	4.57	[20]
Pineapple leaves	600	1:1 carbon:KOH	850	94.62	4.26	[22]
PTL	600	8 M KOH	850	94.93	3.50	[21]
TCL	700	0.5 M KOH	850	74.49	13.49	[23]

The specific capacitance of activated carbon nanofiber/nanosheet for supercapacitor cells derived from leaves biomass wastes were shown in Table 2. The specific capacitance was evaluated by using

cyclic voltammetry method in two-electrode system at low scanning rate of 1 mV s^{-1} . All monolith samples were prepared without any adhesive materials such as pVdF and PTFE. In general, activated carbon monoliths with nanofiber structures show the higher specific capacitance of the 4 leaves biomass types reviewed. Pineapple leaves have the highest capacitance of 150 F g^{-1} and followed by acacia leaves of 113 F g^{-1} . Nanofiber structure makes it possible to provide active pores suitable for ion diffusion at the electrode/electrolyte interface. However, TCL exhibited an increase in specific capacitance from 25 F g^{-1} to 45 F g^{-1} by changing the structure of nanofiber to nanosheet. Nano-scale sheet structures such may increase open surface area, facilitate the diffusion of electrolyte ions in sheet-to-sheet, and offer more active sites to form electric double layers. These results confirmed that these nanostructures changes could affect the performance of supercapacitor electrodes. Based on this analysis, the leaves biomass wastes is potential for activated carbon with nanostructure especially nanofiber and nanosheet as raw material for symmetric supercapacitor electrode.

Table 2. The specific capacitance of activated carbon electrode derived from various biomass sources

Biomass sources	Nanostructures	Electrode system	Electrolyte	Electrode form	C_{sp} (F g^{-1})	Refs
Acacia leaves	Nanofiber	2-electode	$1\text{M H}_2\text{SO}_4$	Monolith	113	[20]
Pineapple leaves	Nanofiber	2-electode	$1\text{M H}_2\text{SO}_4$	Monolith	150	[22]
TCL	Nanofiber	2-electode	$1\text{M H}_2\text{SO}_4$	Monolith	25	[23]
TCL	Nanosheet	2-electode	$1\text{M H}_2\text{SO}_4$	Monolith	54	[23]
PTL	-	2-electode	$1\text{M H}_2\text{SO}_4$	Monolith	56	[21]

4. Conclusion

It is clear from the results of this study that leaf wastes, especially acacia leaves, pineapple leaves, *terminalia catappa* leaves, and *Pandanus tectorius* leaves have the potential to be activated carbon monoliths with nanofiber/nanosheet structures and as a consequence have improved supercapacitor electrical performance. The KOH activation in one-stage integrated pyrolysis both carbonization and physical activation successfully converted biomass leaves wastes to activated carbon monolith with nanofiber/nanosheet structure. Nanofibers were dominated of 90% of activated carbon monolith of four different leaves wastes such as acacia leaves, pineapple leaves, and TCL except PTL. Interestingly, TCL performed two nanostructures at once including nanofiber and nanosheet.

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References

- [1] Han J, Xu G, Ding B, Pan J, Dou H and MacFarlane D R 2014 Porous nitrogen-doped hollow carbon spheres derived from polyaniline for high performance supercapacitors *J. Mater. Chem. A* **2** 5352–7
- [2] Yang H, Ye S, Zhou J and Liang T 2019 Biomass-derived porous carbon materials for supercapacitor *Front. Chem* **7** 1–17
- [3] González A, Goikolea E, Barrena J A and Mysyk R 2016 Review on supercapacitors: Technologies and materials *Renew. Sustain. Energy Rev* **58** 1189–206
- [4] Rangabhashiyam S and Balasubramanian P 2019 The potential of lignocellulosic biomass precursors for biochar production: Performance, mechanism and wastewater application-A review *Ind. Crops Prod* **128** 405–23
- [5] Burke A 2000 Ultracapacitors: why, how, and where is the technology *J. Power Sources* **91** 37–50
- [6] Abioye A M and Ani F N 2015 Recent development in the production of activated carbon

- electrodes from agricultural waste biomass for supercapacitors: A review *Renew. Sustain. Energy Rev* **52** 1282–93
- [7] González-García P 2018 Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications *Renew. Sustain. Energy Rev.* **82** 1393–414
- [8] Sun Y, Guo S, Li W, Pan J, Fernandez C, Arumugam R and Sun X 2018 A green and template-free synthesis process of superior carbon material with ellipsoidal structure as enhanced material for supercapacitors *J. Power Sources* **405** 80–8
- [9] Su X, Li S, Jiang S, Peng Z, Guan X and Zheng X 2018 Superior capacitive behavior of porous activated carbon tubes derived from biomass waste-cotonier strobili fibers *Adv. Powder Technol* **29** 2097–107
- [10] Jiang W, Pan J and Liu X 2019 A novel rod-like porous carbon with ordered hierarchical pore structure prepared from Al-based metal-organic framework without template as greatly enhanced performance for supercapacitor *J. Power Sources* **409** 13–23
- [11] Cai Y, Luo Y, Dong H, Zhao X, Xiao Y, Liang Y, Hu H, Liu Y and Zheng M 2017 Hierarchically porous carbon nanosheets derived from *Moringa oleifera* stems as electrode material for high-performance electric double-layer capacitors *J. Power Sources* **353** 260–9
- [12] Mary A J C, Nandhini C and Bose A C 2019 Hierarchical porous structured N-doped activated carbon derived from *Helianthus Annuus* seed as a cathode material for hybrid supercapacitor device *Mater. Lett* **256** 126617
- [13] Guo S, Chen Y, Shi L, Dong Y, Ma J, Chen X and Song H 2018 Nitrogen-doped biomass-based ultra-thin carbon nanosheets with interconnected framework for High-Performance Lithium-Ion Batteries *Appl. Surf. Sci* **437** 136–43
- [14] Salakhum S, Yutthalekha T, Chareonpanich M, Limtrakul J and Wattanakit C 2018 Synthesis of hierarchical faujasite nanosheets from corn cob ash-derived nanosilica as efficient catalysts for hydrogenation of lignin-derived alkylphenols *Microporous Mesoporous Mater* **258** 141–50
- [15] Deng L, Zhong W, Wang J, Zhang P, Fang H, Yao L, Liu X, Ren X and Li Y 2017 The enhancement of electrochemical capacitance of biomass-carbon by pyrolysis of extracted nanofibers *Electrochim. Acta* **228** 398–406
- [16] Yang W, Shi Z, Guo H, Guo J, Lei X and Yue L 2017 Study on preparation of nanocarbon fibers from wheat-straw based on electrostatic spinning method and its application in supercapacitor *Int. J. Electrochem. Sci* **12** 5587–97
- [17] Taer E, Taslim R, Mustika W S, Kurniasih B, Agustino, Afrianda A and Apriwandi 2018 Production of an activated carbon from a banana stem and its application as electrode materials for supercapacitors *Int. J. Electrochem. Sci* **13** 8428–39
- [18] Yallappa S, Shivakumar M, Nagashree K L, Dharmaprakash M S, Vinu A and Hegde G 2018 Electrochemical Determination of Nitrite Using Catalyst Free Mesoporous Carbon Nanoparticles from Bio Renewable Areca nut Seeds *J. Electrochem. Soc* **165** H614–9
- [19] Taer E, Handayani R, Apriwandi A, Taslim R, Awitdrus, Amri A, Agustino and Iwantono I 2019 The Synthesis of Bridging Carbon Particles with Carbon Nanotubes from Areca catechu Husk Waste as Supercapacitor Electrodes *Int. J. Electrochem. Sci* **14** 9436–48
- [20] Taer E, Natalia K, Apriwandi A, Taslim R, Agustino A and Farma R 2020 The synthesis of activated carbon nano fiber electrode made from acacia leaves (*Acacia mangium* wild) as supercapacitors *Adv. Nat. Sci. Nanosci. Nanotechnol* **11** 25007
- [21] Taer E, Apriwandi A, Krisman, Minarni, Taslim R, Agustino A and Afrianda A 2018 The physical and electrochemical properties of activated carbon electrode made from pandanus tectorius *J. Phys. Conf. Ser* **1120** 012006
- [22] Taslim R, Dewi T R, Taer E, Apriwandi A, Agustino A and Setiadi R N 2018 Effect of physical activation time on the preparation of carbon electrodes from pineapple crown waste for supercapacitor application *J. Phys. Conf. Ser* **1120** 012084
- [23] Taer E, Afrianda A, Taslim R, Krisman, Minarni, Agustino A, Apriwandi A and Malik U 2018 The physical and electrochemical properties of activated carbon electrode made from

- Terminalia Catappa leaf (TCL) for supercapacitor cell application *J. Phys. Conf. Ser* **1120** 012007
- [24] Chen X, Liu L, Zhang L, Zhao Y, Qiu P and Ruan R 2020 A Review on the Properties of Copyrolysis Char from Coal Blended with Biomass **34** 3996–4005
- [25] Thomas P, Lai C W and Bin Johan M R 2019 Recent developments in biomass-derived carbon as a potential sustainable material for super-capacitor-based energy storage and environmental applications *J. Anal. Appl. Pyrolysis* **140** 54–85
- [26] Sodtipinta J, Ieosakulrat C, Poonyayant N, Kidkhunthod P, Chanlek N, Amornsakchai T and Pakawatpanurut P 2017 Interconnected open-channel carbon nanosheets derived from pineapple leaf fiber as a sustainable active material for supercapacitors *Ind. Crops Prod* **104** 13–20
- [27] Sodtipinta J, Amornsakchai T and Pakawatpanurut P 2017 Nanoporous carbon derived from agro-waste pineapple leaves for supercapacitor electrode *Adv. Nat. Sci. Nanosci. Nanotechnol* **8** 035017
- [28] Wang Y, Li W, Zhang L, Zhang X, Tan B, Hao J, Jian Zhang, Wang X, Hu Q and Lu X 2020 Amorphous cobalt hydrogen phosphate nanosheets with remarkable electrochemical performances as advanced electrode for supercapacitors *J. Power Sources* **449** 227487
- [29] Danish M and Ahmad T 2018 A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application *Renew. Sustain. Energy Rev* **87** 1–21
- [30] Taer E, Pratiwi L, Apriwandi, Mustika W S, Taslim R and Agustino 2020 Three-dimensional pore structure of activated carbon monolithic derived from hierarchically bamboo stem for supercapacitor application *Commun. Sci. Technol* **5** 22–30